# A DRAG-REDUCING AGENT FOR USE IN INJECTION WATER AT OIL RECOVERY

The present invention relates to the use of a drag-reducing agent containing a zwitterionic surfactant and an anionic surfactant in waters containing electrolytes. The agent is very efficient at low contents even in waters having a high electrolyte content and is suitable to be utilized in injection waters at oil recovery.

A crude oil reservoir is formed by a stratum of porous rock or sand covered by a rock layer difficult for the crude oil to penetrate. When the pressure in an oil reservoir declines, it is quite common to inject water, for example sea-water, into the oil well to maintain the pressure and the recovery of oil on a high level. However, the injection of water is hampered by the flow resistance (drag) in the conduits and in the oil reservoir and in order to reduce the drag, it has been suggested to add a drag-reducing additive to the injection water.

Thus, EP 116 779 discloses that copolymers of acrylamide and alkylpoly(etheroxy)acrylate have drag-reducing properties in brine solution. In US 4 489 180 it is described a drag-reducing agent comprising of a complex polymer of a mixture of a cationic polymer and an anionic polymer. The addition of the drag-reducing additive is in Example 2 is 500 ppm. Although poly(amide acrylate) polymers may have good drag-reducing effect at a low concentration, it has also been observed that the polymers have a tendency to form aggregates in the oil reservoir, which causes a substantial drop of the flow of injection water.

It is also known, e.g. from WO 92/13925 and WO 96/28527, that surfactants forming rod-like micelles have good drag-

reducing effects. Thus, WO 96/28527 describes a drag-reducing agent comprising at least one betaine surfactant having an alkyl or acyl group with 10-24 carbon atoms in combination with an anionic surfactant having the general structure

$R_1$-B

where $R_1$ is a hydrocarbon group with 10-24 carbon atoms and B is a group $-\overset{\overset{O}{|}}{\underset{\underset{O}{|}}{S}}OM$ or a group $-O\overset{\overset{O}{|}}{\underset{\underset{O}{|}}{S}}OM$, in which M is a cationic, preferably monovalent group, in a proportion between the betaine surfactant and the anionic surfactant of from 20:1 to 1:2. Preferably the betaine surfactant has the general formula

$$R\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^+}}\text{-}CH_2COO^- \qquad (I)$$

where R is the alkyl group or the group $R'NC_3H_6$- where R′ is the acyl group. However, the amount of the surfactant necessary to obtain an essential reduction of the drag has shown to be above 500 ppm of the water. In addition, the formation of micelles and therewith the reduction of drag is expected to be negatively affected by the presence of large amounts of electrolytes. Thus, this type of drag-reducing agents has not at all been regarded as suitable to be used in injection waters, especially not when the injection water is based on sea-water.

It has now been found that a drag-reducing agent containing certain types of zwitterionic surfactants has a

remarkably good drag-reducing effect at a concentration of 50-400 ppm, preferably 60-300 ppm, at large temperature intervals within the range of 2-70°C even in water with an electrolyte content of 0.01-7%, suitably 0.05-6% by weight. Thus, the drag-reducing agent according to the invention can also with a high efficacy and in low amounts be used in brackish water and sea-water with an electrolyte content of 0.3 to 6% by weight. The surfactants in the drag-reducing agent are also readily soluble in the water at the temperatures in the oil reservoir and do not cause any reduction of the injection water flow due to reduced permeability. On the contrary, tests have shown that the presence of the drag-reducing agents of the inventions in the injection water reduces the pressure drop with about 10%, when measured over a plug of calcium carbonate with a permeability of 1.3 mDarcy at a constant flow rate.

The drag-reducing agent for use according to the invention comprises

a) a zwitterionic surfactant of the formula

$$R_1NHC_3H_6\overset{\displaystyle R_3}{\underset{\displaystyle R_4}{\overset{|}{\underset{|}{N^+}}}}R_5COO^- \qquad \text{(I)},$$

where $R_1$ is acyl group with 12-16 carbon atoms, $R_3$ and $R_4$ are independently of each other an alkyl group of 1-4 carbon atoms or an hydroxyalkyl group of 2-4 carbon atoms and $R_5$ is an alkylene group of 1-4 carbon atoms, preferably $CH_2$ or a group

$$\underset{\displaystyle R_6}{\underset{|}{-CH-}}$$

where $R_6$ is an alkyl group of 1-3 carbon atoms, and

b) a zwitterionic surfactant of the formula

$$R_2NHC_3H_6\overset{\displaystyle R_3 \atop |}{\underset{| \atop \displaystyle R_4}{N^+}}R_5COO^- \qquad (II)$$

where $R_2$ is an acyl group with 18-22 carbon atoms, and $R_3$, $R_4$ and $R_5$ have the meanings mentioned above, and

c) an anionic surfactant of the formulae

$R_7(OA)_nB$ or $R_7E$

or a mixture thereof, where $R_7$ is an aliphatic group of 8-14, preferably 10-12, carbon atoms, A is an alkylene group having 2-4 carbon atoms, n is a number from 1 to 10, B is a sulphate group $OSO_3M$, E is a sulphate group $OSO_3M$ or a sulphonate group $-SO_3M$ and M is a cationic, preferably monovalent group; the weight of a), b) and c) being 20-95% by weight, 0-70% by weight and 1-50% by weight, respectively, based on the total amount of a), b) and c).

In the zwitterionic surfactant of formulae I and II, $R_3$ and $R_4$ are independently of each other suitably methyl or hydroxyethyl, and $R_5$ is suitably methylene. Preferably the zwitterionic surfactants have the formula

$$R_1NHC_3H_6\overset{\displaystyle CH_3 \atop |}{\underset{| \atop \displaystyle CH_3}{N^+}}CH_2COO^- \text{ and} \qquad (III), \text{ and}$$

$$\begin{array}{l} \quad\quad\quad CH_3 \\ \quad\quad\quad | \\ R_2NHC_3H_6N^+CH_2COO^- \\ \quad\quad\quad | \\ \quad\quad\quad CH_3 \end{array} \qquad (IV)$$

where $R_1$ and $R_2$ have the meanings mentioned above.

The group $R_1$ is suitably a linear C-12 or C-14 acyl, but also branched acyl groups could advantageously be used. The acyl group $R_2$ can be either saturated or unsaturated but unsaturated acyl groups are preferred. Suitably the acyl group $R_2$ is derived from vegetable oils, such as soy oil, olive oil, rapeseed oil, linseed oil, safflower oil, sun flower oil, cottonseed oil and tall oil.

The anionic surfactants for use according to the invention are well-known products and so are also their production methods. Preferred anionic surfactants are those where $R_7$ contains 10-12 carbon atoms and for many formulations lauryl sulphate, a lauryl $(oxyethylene)_{1-3}$ sulphates, or lauryl sulphonate, or a mixture thereof, is preferred.

Preferably the drag-reducing agent comprises the component a) in an amount of 20-85% by weight, the component b) in an amount of 10-70% by weight, and the component c) in an amount of 4-35% by weight, calculated on the total weight of a), b) and c).

Ordinary sea-water or brackish water have normally a temperature in the range of 5-35°C, while process-water, sometime also called production water, derived at least partially from the water in the production stream of oil and water from the oil well after the removal of the oil phase, normally has a temperature of 30-65°C.

Fortunately, the temperature window, where the drag-reducing effect is substantial can be regulated by the size of the group $R_1$. Thus $R_1$ preferably contains 12-14 carbon atoms, when the injection water is a seawater having a salt content of 2-6% and a temperature of 5-30°C, and 14-16 carbon atoms, suitably in combination with a zwitterionic surfactant of formula II, when the injection water is a production water based on a sea-water having a salt content of 2-6% and a temperature of 30-65°C.

Apart from the zwitterionic surfactant and anionic surfactants, the water-based system may contain a number of conventional components such as corrosion inhibitors and bactericides.

The present invention will now be further illustrated with the aid of the following examples.

**Example 1**

The drag-reducing properties of different drag-reducing additives were evaluated in a synthetic sea-water containing 568 mmoles of chloride, 482 mmoles of sodium, 54 mmoles of magnesium, 28 mmoles of sulphate, 10 mmoles of calcium and 10 mmoles of potassium per liter water. In the evaluation test, 40 ml of the synthetic sea-water containing the drag-reducing additives were stirred in a 50 ml glass beaker with a magnetic stirrer at a constant speed of 700 r.p.m. and at different temperatures. The inner diameter of the beaker was 40 mm and the stirrer bar was 6 x 20 mm. The absence of a vortex in the water surface or a vortex of maximum 2 mm indicated a considerable reduction of the drag. Without addition of a drag-reducing agent, the vortex was 30 mm.

The following surfactants were used in the tests.

C12APB is a compound of formula I, where $R_1$ is a $C_{12}$ acyl, $R_3$ and $R_4$ are methyl and $R_5$ is methylene;

C14APB is a compound of formula I, where $R_1$ is a $C_{14}$ acyl, $R_3$ and $R_4$ are methyl and $R_5$ is methylene;
C16APB is a compound of formula I, where $R_1$ is a $C_{16}$ acyl, $R_3$ and $R_4$ are methyl and $R_5$ is methylene;
C18APB is a compound of formula II, where $R_1$ is a $C_{18}$ acyl derived from oleic acid, $R_3$ and $R_4$ are methyl and $R_5$ is a methylene;
LinAPB is a compound of formula II, where $R_2$ is an acyl derived from linseed oil, $R_3$ and $R_4$ are methyl and $R_5$ is methylene;
SoyAPB is a compound of formula II, where $R_2$ is an acyl derived from soy oil, $R_3$ and $R_4$ are methyl and $R_5$ is methylene;
CanAPB is a compound of formula II, where $R_2$ is an acyl derived from a rapeseed oil with a low content of erucic acid, $R_3$ and $R_4$ are methyl and $R_5$ is methylene;
C14D is an alkyl betaine of the formula $C_{14}$-alkyl$N^+(CH_3)_2CH_2COO^-$;
C16D is an alkyl betaine of the formula $C_{16}$-alkyl$N^+(CH_3)_2CHCOO^-$;
C10S is a decyl sulphate
C12S is lauryl sulphate
C12EOS is lauryl di(oxyethylene) sulphate, and
C12S03 is a lauryl sulphonate.

In Table 1 below the combinations of zwitterionic surfactants and anionic surfactants, the amounts of the individual surfactants used and the temperature range where the vortex was 2 mm or less.

**Table 1 Combinations of zwitterionic and anionic surfactants and their temperature range with a considerable drag-reduction**

| Test | Zwitterionic compound | | Zwitterionic compound | | Anionic compound | | Temp. range °C |
|---|---|---|---|---|---|---|---|
| | Type | Ppm | Type | ppm | Type | ppm | |
| 1 | C12APB | 200 | - | - | C12S | 27 | 4-35 |
| 2 | C14APB | 200 | - | - | C12S | 30 | 16-46 |
| 3 | C14APB | 100 | - | - | C12S | 15 | 16-50 |
| 4 | C14APB | 200 | - | - | C12EOS | 45 | 12-45 |
| 5 | C14APB | 100 | - | - | C12EOS | 23 | 14-52 |
| 6 | C16APB | 200 | - | - | C12S | 25 | 30-66 |
| 7 | C16APB | 100 | - | - | C12S | 13 | 34-65 |
| 8 | C14APB | 100 | C18APB | 100 | C12S | 20 | 14-60 |
| 9 | C16APB | 100 | C18APB | 100 | C12EOS | 18 | 25-65 |
| 10 | C12APB | 50 | C14APB | 50 | C12EOS | 20 | 11-44 |
| 11 | C14APB | 50 | C18APB | 50 | C12S | 10 | 19-60 |
| 12 | C16APB | 50 | C18APB | 50 | C12EOS | 9 | 25-65 |
| 13 | C14APB | 100 | LinAPB | 100 | C12S | 32 | 4-49 |
| 14 | C14APB | 100 | LinAPB | 100 | C12EOS | 33 | 4-44 |
| 15 | C14APB | 100 | SoyAPB | 100 | C12S | 29 | 5-41 |
| 16 | C14APB | 100 | SoyAPB | 100 | C12EOS | 44 | 5-40 |
| 17 | C14APB | 50 | LinAPB | 50 | C12EOS | 16 | 7-42 |
| 18 | C16APB | 50 | LinAPB | 50 | C12S | 21 | 36-60 |
| 19 | C14APB | 58 | CanAPB | 18 | C12S | 14 | 6-50 |
| 20 | C14APB | 38 | CanAPB | 19 | C12S | 9 | 7-45 |
| 21 | C14APB | 100 | CanAPB | 100 | C10S | 39 | < 4-44 |
| 22 | C14APB | 50 | CanAPB | 50 | C10S | 25 | < 4-44 |
| 23 | C14APB | 140 | CanAPB | 60 | C12SO3 | 35 | 4-48 |
| 24 | C14APB | 70 | CanAPB | 30 | C12SO3 | 18 | 4-47 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| A | C18APB | 200 | - | - | C12S | 20 | 27-49 |
| B | C18APB | 200 | - | - | C12EOS | 20 | 29-50 |
| C | C18APB | 100 | - | - | C12EOS | 10 | 40-51 |
| D | LinAPB | 100 | - | - | C12S | 15 | 20-30 |
| E | SoyAPB | 100 | - | - | C12S | 13 | No effect |
| F | C14B | 200 | - | - | C12EOS | 0-200 | No effect |
| G | C14B | 100 | LinAPB | 100 | C12EOS | 0-200 | No effect |
| H | C16B | 100 | LinAPB | 100 | C12S | 0-200 | No effect |
| I | C16B | 100 | LinAPB | 100 | C12EOS | 0-200 | No effect |

From the results obtained it is evident that an agent according to the invention has an excellent drag-reducing effect at dosages below 250 ppm.

**Example 2**

Drag-reducing agents containing C14APB and CanAPB in equal amounts and C12S in varying amounts were tested in injection waters containing different amounts of the synthetic salt described in Example 1. In one test, production water from the North Sea was used. The tests were performed in the same manner as in Example 1. The following results were obtained.

Table 2 Efficacy of drag-reducing agents in injection waters of different salt contents

| Test | C14APB+CanAPB ppm | C12S ppm | Salt content % | Temp. range °C |
|---|---|---|---|---|
| 25 | 200 | 35 | 0.03 | < 5-58 |
| 26 | 100 | 18 | 0.015 | < 5-50 |
| 27 | 200 | 35 | 0.6 | < 5-47 |
| 28 | 100 | 40 | 0.6 | < 5-46 |
| 29 | 200 | 22 | 1.0 | < 5-46 |
| 30 | 100 | 40 | 1.0 | < 5-46 |
| 31 | 200 | 35 | 3.0 | < 5-47 |
| 32 | 100 | 18 | 3.0 | < 5-47 |
| 33 | 200 | 38 | ~ 3.0 [1)] | < 5-51 |
| K | 200 | 0-200 | 0.00 | No effect |

[1)] Production water from the North Sea containing less than 20 ppm of hydrocarbons

The results clearly show that the drag-reducing agents of the present invention have an essential effect in injection waters with different contents of electrolyte.